The Feasibility of Predicting Properties of Oxidizers by Quantum Chemical Calculations

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ABSTRACT

The objective of this research is to gain insight into the fundamental bonding and behavior of energetic N, O, F compounds. Such questions as relative stabilities of N, O, F compounds, possible existence or non-existence of new species, ionization potentials, electron affinities, π-bonding, and charge distribution of these species have been investigated by performing LCAO-MO calculations using a gamut of theoretical techniques (both semi-empirical and rigorous) and analyzing the resulting calculated wave functions, energy levels, charges and bond orders for their pertinence to the above topics.

From these calculations it has already been possible to: 1) predict correctly the greater stability of cis-N_2F_2 relative to trans-N_2F_2; 2) predict the correct order of the differing N-F bond lengths in such diverse species as NF_2, NF_3, trans-N_2F_2 and cis-N_2F_2 and of the differing N-N bond lengths in cis- and trans-N_2F_2 (prior to knowledge of the experimental electron diffraction measurements of N_2F_2 bond lengths); 3) predict the correct order of the symmetric N-F stretch frequencies in NF_2, NF_3, trans-N_2F_2, N_2F_4 and cis-N_2F_2; 4) reproduce by calculations the experimental ionization potential of NF_2; 5) verify the supposition of π-bonding in NF_2 and NF leading to a greater N-F bond dissociation energy in these species than in NF_3.

INTRODUCTION

The objective of our research is to investigate the theoretical and quantum chemistry of energetic N, O, F compounds with the aim of providing insight into the fundamental bonding and behavior of these species so necessary for the guidance and planning of the overall experimental research project in the oxidizer field.

The first question we asked ourselves at the inception of this research was -- what are really the most important fundamental problems to be faced in the program in high-energy oxidizers. To us it seems that one of the most over-riding problems is the question of energetics -- will or will not a particular molecule be stable or perhaps so unstable it can never be isolated; and further -- what can be predicted about dissociation paths and dissociation energies of molecules. In order to tackle the problem of molecular energy calculations by what we feel is the only realistically valid approach, we have undertaken rigorous non-empirical LCAO-MO-SCF calculations of N, O, F compounds in which we shall incorporate correlation and relativistic energy corrections. I shall discuss these more fully in a moment.

However, for these compounds there are many other properties of interest for which solutions using approximate wave functions may yield results of sufficient accuracy to permit interpretation of the desired phenomena. For this reason we have also undertaken research in semi-rigorous calculations with the goal of deriving methods correctly based on the many-electron Hamiltonian but with simpli-

fying approximations for the core and integrals which will make the calculations tractable at least for medium-sized polyatomic molecules. We have also modified the semi-empirical "extended Hückel method" to include a more justifiable physical interpretation of the matrix elements as well as iterative processes which introduce a measure of self-consistency. I shall discuss this latter method in detail later, present some results of the calculations and show their good agreement with experiment.

Rigorous Calculations

The calculational technique used for the rigorous calculations is based on Roothaan's SCF method for closed- and open-shell systems.[1] Molecular orbitals are constructed as linear combinations of atomic orbitals

$$\Phi_i = \sum_\mu c_{i_\mu} \chi_\mu$$

and a configurational wave function Φ_n is represented by an antisymmetrized product wave function. There are two choices for the form of the basis atomic orbitals which are most in current usage

$$\text{Slater orbitals} \quad \chi = (2\zeta)^{n-1}(2n!)^{-1/2}\, r^{n-1}\, e^{-\alpha r}\, \Theta_{\ell,m}(\theta)\Phi_m(\varphi)$$

$$\text{Gaussian orbitals} \quad X = r^{2k} x^{\ell} y^{m} z^{n}\, e^{(-\alpha r^2)}\, \Theta_{\ell,m}(\theta)\Phi_m(\varphi)$$

Slater orbitals are better approximations to the form of actual atomic orbitals and atomic wave functions composed of sums of Slater orbitals for each atomic orbital (rather than minimal basis sets which represent each atomic orbital by a single Slater function) have been shown to be good approximations to the true atomic wave functions and to reproduce quite accurately the atomic Hartree-Fock energies. Even atomic orbitals where each atomic orbital is represented by only two Slater orbitals (the double ζ technique) combine to give fairly good approximations to the atomic wave functions[2] (although for molecular wave functions where one wishes to calculate dissociation energies one must use better than a double ζ treatment and must include some higher orbitals to allow for atomic distortion upon molecular formation[3]. All improvements to the "best-atom" wave functions increase the binding energy since they represent increased flexibility in the orbital basis set for the molecule.) The great problem in using Slater orbitals for polyatomic molecular calculations is the lack of general computational expressions for most of the three- and four-center integrals involved.

The other alternative is to use Gaussians[4] as the basis functions for the atomic orbitals. A paper by Boys in 1956[4] pointed out that a set of Gaussian functions of the form shown is complete and that the required integrals involving these Gaussians (including three- and four-center ones) can be expressed as explicit formulas. Recent calculations by Moscowitz[5] and Harrison[6] and Krauss[7] have shown that molecular wave functions based on Gaussians (GF's) can be made comparable to those based on Slater orbitals (STO's), but for similar energy values about twice as many GF's as STO's are necessary. Since our main interest is in polyatomic systems for which, as yet, three and four-center Slater integral routines are not available, we are concentrating at present on performing our rigorous molecular calculations using basis Gaussian orbitals. We have been very fortunate, through the cooperation of Dr. Moscowitz, of New York University, (formerly of MIT) in

having the MIT POLYATOM program (rigorous SCF calculations based on Gaussian orbitals) made available for our research here at RIAS and additional supplementary routines for POLYATOM have been written at RIAS. As far as orbital energies go, calculations at MIT indicated that the Gaussian bases seem to give excellent results. Therefore, we have proceeded to explore SCF Gaussian calculations for NF compounds.

Before I mention our preliminary results to date on the Gaussian SCF calculations of NF compounds, I should just like to indicate how correlation and relativistic energy corrections will enter into the estimation of dissociation energies of NF compounds.

Correlation and Relativistic Effects

$$E_{exact} = E_{HF} + E_C + E_R$$

which holds for any state of any atomic or molecular system. E_{exact} is the actual energy of the state, E_{HF} is the computed Hartree-Fock energy for the state (accounting for 99 or more of E_{exact}), E_C is the correlation energy in the state (a correction term accounting for the deficiency in the Hartree-Fock model - the antisymmetrized product form of the wave function and the Pauli exclusion principle take into account most of the correlation between electrons of like spin - but none between electrons of opposite spin) and E_R is the relativistic energy in the state (which in this definition includes spin-orbit coupling effects in addition to true relativistic effects). In calculations by Clementi[8], McLean[9] and Yoshimine[10] on such diatomic molecules as HF, LiF, BeO, it was found that the net contribution of correlation energy to the molecular binding energy (molecule minus separated neutral atoms) was very nearly equal to the correlation energy difference between the atoms separated so as to maintain the structure of electron pairs in the molecule (for example HF giving F^- and H^+ at infinite separation) and the neutral atoms in their ground states. Alternatively the correlation energy was quite close to the difference between that of a united atom corresponding to the diatomic and the neutral atoms in their ground states. Professor Sinanoglu[11] has shown that pair correlations are nearly additive and he has calculated some of these correlations non-empirically for first row atoms. Thanks especially to the work of Clementi[12] there is now a great deal of empirical knowledge of correlation energies of first and second row atoms. The lament current some few years ago (that molecular orbital wave functions would never be good enough to calculate reliably dissociation energies) is now being replaced by the more optimistic statement that the results of Hartree-Fock molecular calculations combined with empirical knowledge of correlation energies can lead to accurate predictions of dissociation energies of molecules. Considering that the entire molecular extra correlation energy (of the order of 1.7 ev per bond) contributes directly to the dissociation energy and bond dissociation energies are only about 2 to 4 ev one sees why 1) correlation energy must be taken into account and 2) why we must strive for accurate wave functions.

N-F Results

The closed-shell POLYATOM program is operational and can handle up to 50 basis orbitals. We have already run a test of NF_3 with a minimal basis set for N and F of 3s and one each p_x, p_y, p_z orbitals to check it out. The ordering of the energy levels was as anticipated, first the four inner shell orbitals, then above them levels which may be associated with the three bonds and the lone pairs on fluorine; the highest occupied orbital finally corresponds

closely to the lone pair on nitrogen. Of course, due to the fact that the basis used was minimal the calculated energy was too high. In order to improve the accuracy of the wave function, the orbitals characterizing the gaussians had to be varied and the basis expanded. We then ran calculations on NF itself with larger basis sets in order to optimize the parameters for N and F in molecular combination.

At present we are performing these calculations on NF_2 and NF_3 and in the immediate future we shall calculate cis- and trans-N_2F_2 and N_2F_4.

We shall continue our research on these rigorous calculations of NF compounds until we have satisfactorily been able to reproduce the dissociation energy of an NF compound -- probably NF_3 since this is the simplest NF molecule whose heat of formation and first bond dissociation energy have been measured directly. It was actually the apparently anomolous pattern in bond dissociation energies of NF which led originally to our theoretical interest in NF compounds. In 1961 at an American Chemical Society Symposium on Chemical Bonding in Inorganic Systems, Dr. Colburn of Rohm and Haas at Huntsville made mention of the fact that while the N-H dissociation energies in NH_3 were $D(H_2N\text{-}H) > D(HN\text{-}H) > D(N\text{-}H)$ in NF_3 the order was $D(F_2N\text{-}F) < D(FN\text{-}F)$. We postulated at that time that the reason must in large part be due to the fact that although there is virtually no π-bonding in NF_3, there must be a considerable amount of $F \rightarrow N$ π-bonding in NF_2 which is planar.[13] (Our subsequent calculations have confirmed this $F \rightarrow N$ π-bonding in NF_2). π-bonding in NF_2 would increase the N-F bond strength over that in NF_3. The closeness of ionization potentials of NF_2 and NH_2 were also both predicted to be due to $F \rightarrow N$ π-bonding in NF_2 and NF_2^+. (Incidentally, there must also be $F \rightarrow N$ π-bonding in N-F).

Semi-empirical Calculations

Good rigorous SCF calculations on polyatomic molecules are long, difficult and tedious to program, and inevitably expensive in computer time. What was needed was a simple semi-empirical approximate method for three-dimensional molecular orbital calculations.

In recent years increasing use is being made of an extended Hückel type LCAO-MO-SCF method for calculation of wave functions and energies of three-dimensional molecules (as opposed to molecules having separable π-systems). This extended Hückel-type method is based on a technique apparently originally introduced by Wolfsberg and Helmholz[14] and used over the years by Longuet-Higgins[15], extensively by Lipscomb and co-workers[16] especially Hoffman, as well by Ballhausen and Gray[17]. From a molecular orbital Φ_i built up as a linear combination of atomic orbitals χ_μ

$$\Phi_i = \sum_\mu c_{i_\mu} \chi_\mu$$

and applying the variation principle for the variation of energy the following set of equations for the expansion coefficients is obtained

$$(\alpha_\mu + ES_{\mu\mu})c_\mu + \sum_{\mu \neq \nu} (\beta_{\mu\nu} - ES_{\mu\nu})c_\nu = 0 \qquad \nu = 1,2,\text{--}M \text{ where M is the number of atomic orbitals}$$

E = energy

$S_{\mu\nu} = \int \chi_\mu^* \chi_\nu \, dv$ = overlap integral

$H_{\mu\mu} = \alpha_\mu = \int \chi_\mu^* H \chi_\mu \, dv$ = Coulomb integral

$H_{\mu\nu} = \beta_{\mu\nu} = \int \chi_\mu^* H \chi_\nu \, dv$ = Resonance integral $\mu \neq \nu$

H is an effective one electron Hamiltonian representing the kinetic energy, the field of the nuclei and the smoothed-out distribution of the other electrons.

The diagonal elements are set equal to the effective valence state ionization potentials of the orbitals in question. The off-diagonal elements, $H_{\mu\nu}$, can be evaluated in several ways:

1) In the early work on the boron hydrides the relationship

$H_{\mu\nu} = K'S_{\mu\nu}$ with $K' = -21$ ev was used. However one was forced to use inordinately high values of K' due to the requirement that K' be smaller than any diagonal matrix element. (L-H+R [15])

2) A better-approximation was to set

$H_{\mu\nu} = 0.5K (H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}$ and to use $K = (1.75 - 2.00)$ (W-H [14])

3) A similar expression

$H_{\mu\nu} = K'' (H_{\mu\mu} \cdot H_{\nu\nu})^{1/2} S_{\mu\nu}$ which differs only in second order and has certain computational advantages has also been used. (B-G [17])

4) Cusachs reported at the Sanibel Quantum Chemistry Conference last winter[18] that the repulsive terms in the W-H model which assume electron repulsion and nuclear repulsion to cancel nuclear-electron attraction, consist of one-electron anti-bonding terms only. Cusachs noted that Ruedenberg observed that the two-center kinetic energy integral is proportional to the square of the overlap integral rather than the first power. We shall comment further on this point later - since we think there may be a slightly different interpretation. However, Cusachs used to develop the approximation

$$H_{\mu\nu} = \frac{(H_{\mu\mu} + H_{\nu\nu})}{2} S_{\mu\nu} (2 - S_{\mu\nu})$$

which contains no undetermined parameters and avoids collapse.

5) At Istanbul Professor Fukui[19] also reported a new scheme

$$H_{\mu\nu} = \left\{ \frac{1}{2} \left(H_{\mu\mu} + H_{\nu\nu} \right) + K \right\} S_{\mu\nu}$$

for approximating the off-diagonal elements.

Since the valence state ionization potentials are known to be functions of the electron population at that atom we have introduced iterative schemes for the calculation of $H_{\mu\mu}$ such as:

a) $$\alpha_{\mu_a}^{R} = H_{\mu_a\mu_a}^{R} = H_{\mu_a\mu_a}^{R-1} - \left(m_{\mu_a} - q_{\mu_a}^{R-1} \right) W$$

where R is the iteration cycle number, μ_a refers to orbital a on atom μ, m_{μ_a} is the occupation number for that orbital in the ground state and q_{μ_a} is the electron population on that atom in the molecule.

b) $$\alpha_{\mu_a}^{R} = H_{\mu_a\mu_a}^{R} = H_{\mu_a\mu_a}^{R-1} + A_{\mu_a} q_{\mu_a}^{R-1} + B_{\mu_a} \left(q_{\mu_a}^{R-1} \right)^2$$

which follows a Glockler-type equation and where $\alpha_{\mu_a}^{0}$ is equal to the valence state ionization potential. The iterative cycles are continued until

$$\left| q_{\mu_a}^{R-1} - q_{\mu_a}^{R} \right| < \text{constant}$$

The off-diagonal elements can be constructed in accordance with any of the schemes indicated earlier.

Preliminary calculations of the extended Hückel-type on NF and OF compounds have led to a number of interesting and fruitful observations.

Compound	N-F Distance (Å)	N-F Symmetric Stretch cm^{-1}	Calculated N-F Overlap Population
NF_2	1.365	1074	0.45
NF_3	1.371	1031	0.41
N_2F_2-trans	1.398	1010	0.37
N_2F_2-cis	1.409 (Bauer) 1.384 (Other research)	896	0.34

Quite striking is this table comparing our calculated N-F overlap populations with experimentally measured N-F bond lengths, N-F symmetric stretch frequencies and N-F bond dissociation energies. In this table are shown our original calculations which were performed using Sanborn's estimate for the geometry of N_2F_2 in which N-F and N-N bond distances were considered to be the same for both the cis- and trans-isomers. Our calculational results based on overlap population indicate quite clearly that the N-F distance in trans-N_2F_2 should be shorter than that in

cis-N_2F_2 -- and this point was experimentally verified by Professor Simon Bauer at Cornell. Professor Bauer sent us his student's unpublished results on electron diffraction measurements of NF compounds, and asked for our theoretical interpretation of the differing N-F bond lengths. The fact that our calculated N-F overlap populations, even when using the original Sanborn estimate of identical N-F bond lengths for cis- and trans-N_2F_2, are capable of predicting correctly the order of the experimentally measured bond distances PRIOR to our knowledge of Professor Bauer's results is very encouraging. The situation seems to be similar to that explored years ago in Hückel calculations of aromatic hydrocarbons. In condensed ring systems it is possible to do an original Hückel LCAO-MO π-electron calculation assuming all bond lengths equal. From the resulting differences in calculated bond orders it is possible to predict that certain of the bonds in the rings differ in length from the others. Refined calculations can then be made using differing values of β in order to predict more closely other properties of the molecules. The correlation of overlap population with bond length even seems capable of enabling one to evaluate the validity of experimental measurements. For example, the calculated N-F overlap population in cis-N_2F_2 of 0.34 compared to 0.37 for trans-N_2F_2 would indicate that the N-F distance of 1.409 A for cis-N_2F_2 as measured by Bauer is more reasonable compared to 1.398 A for trans-N_2F_2 than is the value of 1.384 A measured by another investigator. Also the order of N-F dissociation energies is entirely compatible with the order of their calculated overlap populations. Bauer also observed differences in the N-N distances in cis- and trans-N_2F_2 and these differences are also reproduced by our original calculations.

	N=N Distance A	Calculated N-N Overlap Population
cis-N_2F_2	1.209	1.29
trans-N_2F_2	1.224	1.19

Professor Bauer noted that the shorter N=N distance in cis-N_2F_2 is entirely compatible with the greater thermochemical stability of the cis-N_2F_2. Also, our calculated total energies for

cis-N_2F_2	-535.83 ev
trans-N_2F_2	-534.80 ev

confirm the experimental order of thermal stabilities

$$\text{cis-}N_2F_2 > \text{trans-}N_2F_2$$

A further discussion of some of the salient results of these particular species is elucidating. For NF_2 we had also performed a Pariser-Parr-Pople-type SCF open-shell[21,22] (including electron repulsion) calculation for the π-orbitals only of NF_2 assuming that the unpaired electron and a pair of electrons on each fluorine were in a π-orbital with a node in the plane of the molecule. We reasoned that if we were fortunate enough to make reasonable approximations for the core, the appropriate valence state ionization potentials and the electron repulsion integrals, we might arrive at a nearly correct value for the calculated ionization potential of NF_2 which we could check with the experimentally measured value. Applying the usual correction factor necessary for π-electron ionization potentials calculated by the Pople-SCF method, we calculated the ionization

potential of NF_2 to be 11.83 ev, in excellent agreement with the experimentally measured value of 11.8 ev. When one is dealing with open-shell species, the ionization potential is no longer equal to the negative of the orbital energy of the highest occupied molecular orbital but instead must be calculated from the differences in the total energies of the species and its positive ion. (The same holds true in calculating electron affinities.) This is because, due to the coupling terms between open- and closed shells in the species, one solves two pseudo-eigenvalue equations. Without applying any correction factors, we calculated the the electron affinity of NF_2 as 1.64 - this quantity is as yet unmeasured.

The results of the three-dimensional Hückel calculation also indicated that the highest occupied molecular orbital (HOMO) (which was singly filled) was indeed a π-type orbital in the NF_2 radical. This would lend support to the validity of computing the ionization potential from the Pople-SCF π-electron energies.

N_2F_2

Three-dimensional Hückel calculations led to the interesting correlation with stretching frequencies shown earlier, trans-N_2F_2 having both a greater stretching frequency and bond order than cis-N_2F_2. Whereas the N-F π-bond orders for these two isomers are nearly identical the total overlap populations are significantly different.

We had also performed Pariser-Parr-Pople-SCF π-electron only calculations on the two N_2F_2 isomers. The coefficients of the atomic orbitals in the four π-type molecular orbitals of the three-dimensional treatment are extremely close to the coefficients obtained in both the Hückel-π and Pople-SCF π-electron only calculations on both isomers. The calculations also indicate that the HOMO is not a π-type orbital; however lying immediately above and below the HOMO are two π-type orbitals.

NF_3

From the three-dimensional Hückel calculations the order found for the orbital energies agrees with that expected: above the four inner-shell levels which may be associated with the three bonds and the lone pairs on fluorine; the highest occupied level, finally, corresponds to the lone pair on nitrogen. This is exactly the same order found in our rigorous SCF calculation using gaussian basis orbitals.

Thus, for general descriptions of bonding in N-F compounds a three-dimensional Hückel treatment leads to results consistent with the properties and behavior of known NF compounds and thus gives promise of being applicable to the prediction of the properties of new compounds.

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